

DIFFERENT ROUTES FOR PRODUCTION OF ACETIC ACID –A CASE STUDY

G.B. Kumbhar¹, M.A. Suryawanshi², Amarsinh Ghatge³, Shreyas Ghodinde⁴, Sagar Patil⁵

^{3,4,5}B.E. Student, Dept. of Chemical Engineering, Bharati vidyapeeth college, Maharashtra, India

^{1,2}Professor, Dept. of Chemical Engineering, Bharati vidyapeeth college, Maharashtra, India

Abstract – The World production of acetic acid is about 9 million tons. Acetic acid commonly known as ‘vinegar’ is very important chemical. So the production of acetic acid through more efficient way is very important. It can be produce by four different routes namely, anaerobic fermentation route, direct oxidation of n-butane, acetaldehyde oxidation route, methanol carbonylation route. The production of acetic acid through methanol carbonylation route is found to be more economical and the corresponding liquid phase reactions easy to control

Key Words: Production of Acetic Acid, Methanol Carbonylation Route

1. INTRODUCTION

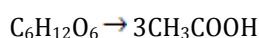
Acetic acid (AA) usually called vinegar is an important commodity used in chemical industries with about 9million tons of world demands per year. The main use of this chemical is in the manufacture of assorted acetate esters, fungicide organic compound, organic solvent and preparation of pharmaceuticals. Acetic acid [CH₃COOH] is a corrosive organic acid having sharp odour and pernicious blistering properties.

The 99.8% pure acetic acid commonly called glacial acetic acid can be produced by four major routes.

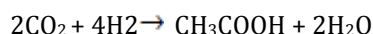
1. Acetic acid by anaerobic fermentation route.
2. Acetic acid by direct oxidation of N- Butane.
3. Acetaldehyde oxidation route.
4. Methanol carbonylation route.

1.1 Anerobic Fermentation

In these process species of anaerobic bacteria including member of acetobacterium are used to convert sugars to acetic acid directly without using ethanol as intermediate.



These acetogenic bacteria can produce acetic acid from one carbon compounds, including methanol, carbon monoxide.

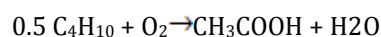


At present, this method is still more cost effective than other fermentation method.

1.2 Acetic Acid by Direct Oxidation of N- Butane

The oxidation reaction of N-butane to acetic acid can be carried out in three different ways

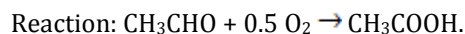
1. A vapour phase non-catalytic reaction at 350 to 400°C and 5-10 atm. pressure.
2. A liquid phase non-catalytic reaction at 160 to 180°C and 45-55 atm. pressure.
3. A liquid phase homogeneous catalytic reaction at 160-180°C and 45-55 atm. pressure



This method is been in commercial operation since 1911 in Germany and 1920 in USA.

1.3 Oxidation of Acetaldehyde

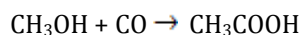
The 1stcommercialized process that came into practice for production of AA was oxidation of acetaldehyde. This process uses catalyst which is heterogeneous in nature of manganese or cobalt acetate with the reactants of acetaldehyde and oxygen.



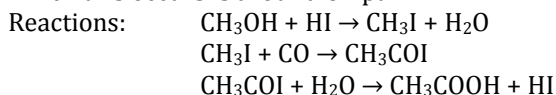
In the reactor, acetaldehyde is introduced from the head and the oxygen needed for oxidation is passed from bottom. In this process temperature plays a vital role for oxidation. It should be maintained 270C for 1st hrs. Then increase of 1 to 20C for 2hrs and gradually increased up to 600C after 4hrs. The most satisfactory operating temperature is about 600C. The reaction takes 12-14hrs for completion. The pressure was kept below 5 kg/cm². The whole process takes 12-14 hrs to complete. The heat of reaction in reactor is removed using cooling systems.

1.4 Liquid – phase Methanol Carbonylation Route.

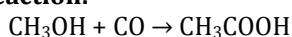
Methanol- carbonylation route is the best way and hence it is used largely on industrial level for manufacturing of AA. It accounts for 75% of the world's acetic acid production technologies. In this process excess of CO used with methanol, and equilibrium can be increased by increasing pressure & vice versa in reaction temperature through the following reaction:



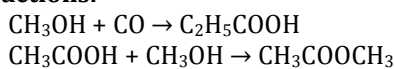
It is clearly seen that C-O bond has to be added to methanol molecule to give AA. This is done using additives like halogen promoters most common is HI, to activate the C-O bond on methanol. At atmospheric pressure the required temperature for converting methanol into AA is around 300°C. In order to reduce the reaction temperature around 150-200°C homogeneous catalysts are used. The pressure at which this occurs is around 6 MPa.



Main reaction:



Side Reactions:



Major companies use different metal-organic complex catalysts like cobalt, rhodium, iridium etc for manufacturing of AA. In the late 1990s, the chemicals company BP Chemicals commercialized the Cativa catalyst ($[\text{Ir}(\text{CO})_2\text{I}_2]^-$), which is promoted by ruthenium. This iridium catalyzed process is greener and more efficient and the best way for manufacturing AA. Fig. 1 is the catalytic cycle for the carbonylation of methanol using iridium as the catalyst.

2. ADVANTAGES OF LIQUID – PHASE CARBONYLATION PROCESS:

- For Cativa process the selectivity is 99% whereas it is 90% for acetaldehyde oxidation process and less for other processes.
- The operation is economical and cheaper as compared to other processes.
- The methanol used as the feed is comparatively cheaper than the feed in other processes.
- Fermentation process which also seems viable in terms of operation involves a greater upstream and downstream cost for sterilization of equipment to provide an environment for microbial growth.
- The liquid phase reaction is easy to control.

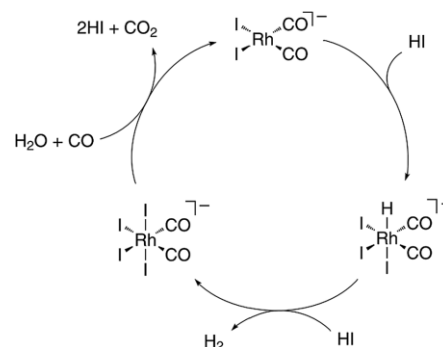


Fig. 1 Catalytic cycles of rhodium complexes during AA synthesis and WGS reaction [4]

Table 1: Commercialized processes for a liquid-phase methanol carbonylation to AA

	BASF	Monsanto	Cativa
Catalyst Type (metal-organic complex)	Cobalt/Mel	Rhodium	Iridium
Promotor	-	-	CH ₃ I, H ₂ O
Temperature (°C)	230	150-200	190
Pressure (MPa)	6-8	3-6	2.8
Yield (methanol based, %)	90	99	>90
Main Byproducts	Methane, acetaldehyde, ethanol and ether	-	Propionic acid, Methyl acetate

3. CONCLUSION

Acetic acid can be synthesized from various feedstocks through various methods/process like acetaldehyde oxidation, hydrocarbon oxidation, anaerobic fermentation and methanol carbonylation. Compared with other routes methanol carbonylation (cativa process) has been the most promising technology for synthesis of AA. Various metal-organic complex catalysts are used in liquid –phase process

to ease up the process. Iridium based homogenous catalyst is use in cativa process. At industrial scale around 75% acetic acid is produced using the above mention process.

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